

Theoretical prediction of Jahn-Teller distortions and orbital ordering in $\text{Cs}_2\text{CuCl}_2\text{Br}_2$

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With the use of the density function calculations we show that the actual crystal structure of $\text{Cs}_2\text{CuCl}_2\text{Br}_2$ should contain elongated in the ab -plane CuCl_4Br_2 octahedra, in contrast to the experimentally observed compression in c -direction. We also predict that the spins on Cu^{2+} ions should be ferromagnetically ordered in ab -plane, while the exchange interaction along c -direction is small and its sign is uncertain.

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I. INTRODUCTION

The system $\text{Cs}_2\text{Cu}(\text{Cl},\text{Br})_4$ attracts a lot of attention mainly because of its unconventional magnetic properties. Cs_2CuBr_4 is the only triangular-lattice antiferromagnet, which exhibits unusual quantum magnetization plateau, [1] while Cs_2CuCl_4 shows field-induced Bose-Einstein condensation of magnons. [2] Thus the investigation of intermediate compositions of $\text{Cs}_2\text{CuCl}_{4-x}\text{Br}_x$ may not only shed some light on the magnetic properties of both compounds, but may also results in the discovery of new phenomena.

The mixed $\text{Cs}_2\text{CuCl}_{4-x}\text{Br}_x$ crystal series was successfully grown at 50 °C with orthorhombic crystal structure. However, at room temperature in the synthesis process the stabilization of a new tetragonal phase for $1 < x < 2$ was observed. [3]

The crystal structure of tetragonal specimens consists of the CuCl_2 layers stacking in the c -direction and divided by the Cs and Br atoms, see Fig. 1. It is important to mention that Cu ions in one of the layers placed on a top/bottom of the void between CuCl_4 plaquettes of another layer. According to Ref. 3, the Cl and Br ions form octahedra surrounding Cu with two short, apical, Cu-Br and four long, planar, Cu-Cl bonds. Such kind of the compressed octahedra are quite untypical for the Jahn-Teller Cu^{2+} ions with d^9 electronic configuration for the dense crystal structures, and the authors of Ref. 3 mentioned that the real type of distortions may be hidden by the multidomain structures.

There are a lot of insulating materials, where ligand octahedra surrounding Jahn-Teller active metal ion turn out to be elongated: KCrF_4 [5, 6], Cs_2AgF_4 [7, 8], K_2CuF_4 [9, 10], and others, while there are only few systems with the opposite distortion. Generally speaking there can be different mechanisms, which stabilize elongated octahedra. [11] One of the reasons can be the gain in the magnetic energy due to more efficient hoppings

between half-filled $x^2 - y^2$ -like and oxygen p -orbitals in the case of the d^9 configuration. Another one is related with the features of the elastic interactions. It can be shown that the total energy of elongated octahedra is lower than compressed if in the expression for the elastic energy the terms of higher order than quadratic are taken into account. [12]

In the present paper, using ab-initio band structure calculations, we found that the crystal structure of $\text{Cs}_2\text{CuCl}_2\text{Br}_2$ ($x = 2$), which corresponds to the lowest total energy, indeed corresponds to the elongated CuCl_4Br_2 octahedra. This is in contrast to the observed experimental structure, [3] but support general tendency in the Jahn-Teller distortions to stabilize elongated, not compressed octahedra. The more detailed structural study should be carried out to confirm (or disprove) the

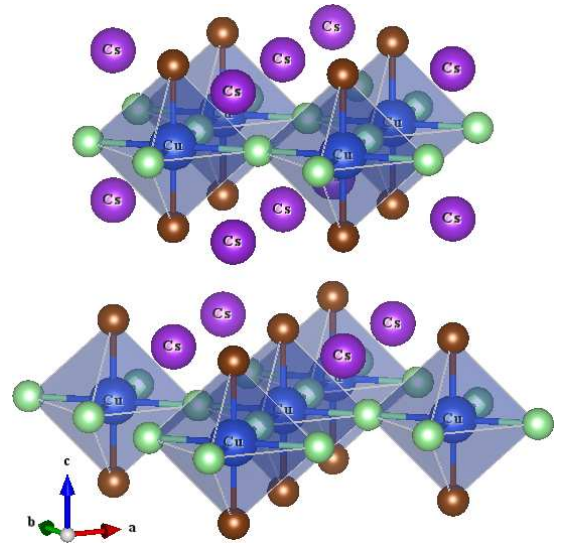


FIG. 1: (color online). The crystal structure of the tetragonal phase of $\text{Cs}_2\text{CuCl}_2\text{Br}_2$. Blue balls are Cu ions, light green, brown and purple are Cl, Br and Cs ions respectively. According to Ref. 3, the CuCl_4Br_2 octahedra are compressed along the c -axis. The image was generated using VESTA software. [4]

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TABLE I: Total energies in meV per formula unit for different magnetic configurations for the experimental crystal structure. [3] The energy of the FM configuration was chosen as zero.

	Total energy, meV
FM	0
AFM-A	3.7
AFM-C	2.9
NM	8.8

predicted lattice and orbital ordering.

II. CALCULATION DETAILS

The pseudo-potential PWscf code was chosen for the calculations. [13] We used ultrasoft pseudo-potentials with the nonlinear core correction and the Perdew-Burke-Ernzerhof (PBE) version of the exchange-correlation potential. [14] In order to take into account strong Coulomb repulsion on the Cu sites the GGA+U approximation was utilized. [15] On-site Coulomb repulsion parameter U was chosen to be 7.0 eV, while intra-atomic Hund's rule exchange $J_H = 0.9$ eV. [16]

The charge density and kinetic energy cut-offs equal 40 Ry and 200 Ry, respectively. 144 k -points ($6 \times 6 \times 4$) in a full part of the Brillouin zone for the unit cell, consisting of 4 formula units (f.u.), were used in the self-consistency course. The structural optimization was performed while each component of the force were more than 2 mRy/a.u. No symmetry operations were used in the course of self-consistency.

The crystal structure was taken for $\text{Cs}_2\text{CuCl}_{2.2}\text{Br}_{1.8}$. [3] We used the supercell $\sqrt{2} \times \sqrt{2} \times 2$ cell to allow the simplest types of the orbital ordering.

III. CALCULATION RESULTS

The total energy is known to depend on the type of magnetic ordering, and this magnetic ordering may have an influence on the lattice distortions through the stabilization of the particular orbital ordering. [17] That is why it is important to study possible lattice distortions together with the analysis of the magnetic interactions.

The total energies of the following magnetic configuration were calculated: nonmagnetic (NM), ferromagnetic (FM), AFM-A type (when all ions in ab -plane are ferromagnetically ordered, while the interaction between planes is antiferromagnetic), and AFM-C type (nearest Cu in the ab -plane are AFM ordered, the next nearest neighbors in c -direction are ferromagnetically coupled).

The lowest in energy in the tetragonal crystal structure of Ref. 3 turns out to be the FM configuration (see Tab. I). The analysis of the occupation matrix shows

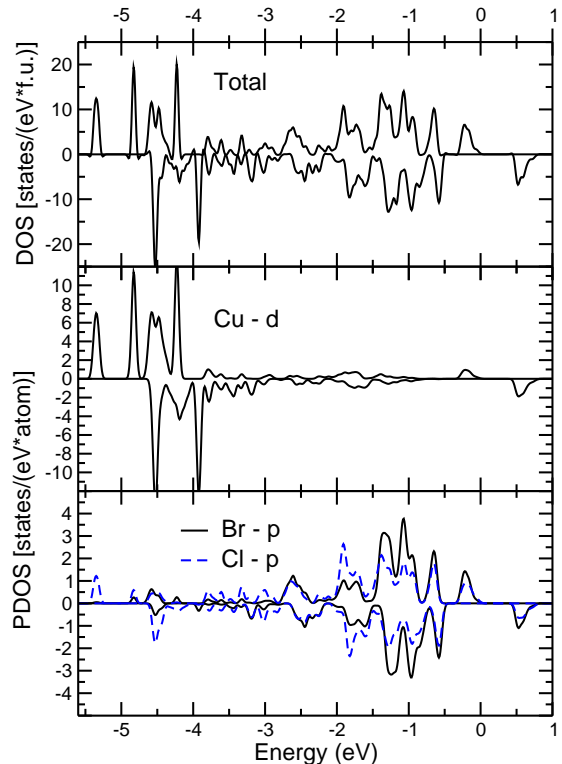


FIG. 2: (color online). The total and partial DOS for FM configuration in the relaxed crystal structure with alternating long and short Cu-Cl bond in the ab -plane. Positive (negative) values correspond to spin majority (minority) states. The Fermi level is set to zero.

that the single hole in $3d$ -shell of Cu^{2+} is localized on $3z^2 - r^2$ -orbital in the FM configuration. Such an orbital filling is obviously a result of the local compression of CuCl_4Br_2 octahedra in the structure of Ref. 3.

The ground state is metallic for any of the investigated magnetic configurations. This is in contrast to the fact that the undoped materials Cs_2CuCl_4 and Cs_2CuBr_4 are Mott insulators [18, 19], and the samples of the intermediate compound $\text{Cs}_2\text{CuCl}_{2.4}\text{Br}_{1.6}$ do not have metallic shine. [3]

The compression of the octahedra in $\text{Cs}_2\text{CuCl}_2\text{Br}_2$ in the c -direction prevents the $x^2 - z^2/y^2 - z^2$ orbital order observed in KCuF_3 [15] and K_2CuF_4 [9, 10], where Cu ions also have one hole in the e_g sub-shell. In order to allow the same type of the orbital pattern and compare total energies of different solutions we tetragonally distorted CuCl_4Br_2 in the ab -plane and relaxed crystal structure with the constrain to keep the same cell volume. In addition we also performed the lattice optimization for the initial non-distorted in ab -plane structure, since the experimental structure not necessarily corresponds to the ground state crystal structure in the cho-

TABLE II: Distances and total energies per formula unit for different magnetic configurations for the relaxed crystal structures. The energy of the FM configuration with two long and two short Cu-Cl bonds was chosen as zero, it is 557.7 meV lower than the FM solution for the tetragonal not relaxed crystal structure.

	Cu-Cl dist., Å	Cu-Br dist., Å	Total energy, meV
FM	$3.02 \times 2 / 2.25 \times 2$	2.55×2	0
FM	2.64×4	2.45×2	285.1
AFM-A	$3.02 \times 2 / 2.25 \times 2$	2.55×2	-0.8
AFM-C	2.64×4	2.44×2	280.6
NM	2.64×4	2.44×2	286.4

sen approximation (GGA+U). In effect we obtained two crystal structures corresponding to the same magnetic order (relaxed initial experimental and relaxed distorted in ab -plane structures). The results are summarized in Tab. II, where the second, forth, and fifth lines refer to structure optimized starting from the lattice presented in Ref. 3 (four equal Cu-Cl distances) and the first and the third lines correspond to the results for the structure with octahedra elongated in ab -plane.

The lowest total energy corresponds to FM and AFM-A type configurations with strongly distorted in the ab -plane CuCl_4 plaquettes, as shown in Fig. 3. The energy difference between these two solutions is tiny and may depend on the details of the calculations, but both lie much lower (~ 558 meV) in energy than the ground state magnetic configuration (FM) for the tetragonal not optimized crystal structure. Moreover, it is clearly seen from Tab. II that only half of this difference can be compensated by the ionic relaxation which does not change a local symmetry of Cu^{2+} ions (i.e. that there are 4 equal Cu-Cl bonds in ab -plane).

The second half of the total energy decrease is related to the distortions in ab -plane such that they do not change the average Cu-Cl bond length, but create checkerboard order of the long and short Cu-Cl bonds. The distortions in the ab -plane are accompanied by a moderate elongation of the CuCl_4Br_2 octahedra in c -direction, Cu-Br bond length increases on ~ 0.1 Å, which is compensated by the Cs-Br bond squeezing. Thus, instead of compressed in c -direction octahedra, the ionic relaxation rather stabilizes the elongated in alternating directions in ab -plane CuCl_4Br_2 octahedra.

Such type of the distortions results in the $x^2 - z^2/y^2 - z^2$ orbital order, like in KCuF_3 , see Fig. 3. This orbital pattern leads to a strong ferromagnetic super-exchange in ab -plane, which stabilizes FM or AFM-A magnetic configurations, which agrees with our total energy calculations.

Finally we present the total and partial density of states (DOS) plots for the distorted in ab -plane relaxed crystal structure, e.g. for FM configuration [Fig. 2)]. Due to a large on-site Coulomb repulsion Cu- $3d$ band goes

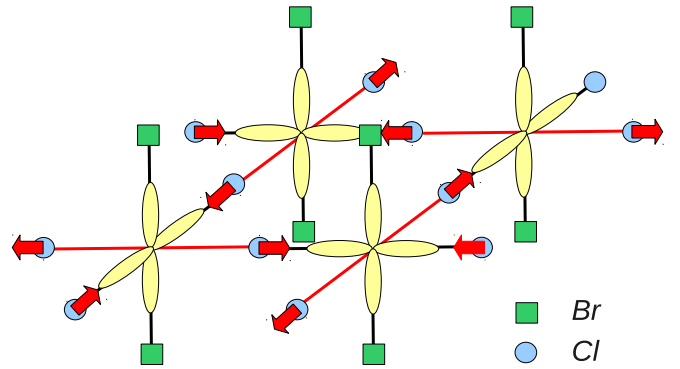


FIG. 3: (color online). The sketch of the proposed orthorhombic distortions corresponding to the lowest total energy in Tab. II, when all CuCl_4Br_2 octahedra are elongated in alternating directions in the ab plane (long Cu-Cl bonds are shown in red) and the orbital order, which is expected for such kind of the distortions (hole orbitals of Cu^{2+} are shown).

away from the Fermi level and is placed mainly in the energy range from -5.5 eV to -3 eV. The Br- p and Cl- p states are concentrated from -3 eV to 1 eV. It is important to note, that in contrast to a naive expectation, the largest contribution to the bottom of the conduction band (as well as to the top of the valence band) comes from Cl- p and Br- p states: ~ 3.6 states/[eV*f.u.], while Cu- d provides only 1.9 states/[eV*f.u.] (the rest belongs to other states of Cu, Cl and Br ions). This means that the hole is actually localized not on the Cu- $x^2 - y^2$ like orbital, but rather on the Wannier orbital, which is centered on the Cu site, has $x^2 - y^2$ symmetry, but also has significant contributions (tails) on the surrounding Cl and Br ions. This is similar to the situation in $\text{Cs}_2\text{Au}_2\text{Cl}_6$, [20] but here the spatial orientation of the Wannier orbital is different. The strong admixture of Cl- p and Br- p states to the conduction band may be the reason of the small band gap value ~ 0.5 eV in the present GGA+U calculations, since these states act as a ballast. We expect that the LDA+ U_{WF} approximation, where U is applied not only on the d -part, but on a whole Wannier function will result in a larger band gap.

Summarizing, on the basis of the ab-initio calculations we have shown that the layered material $\text{Cs}_2\text{CuCl}_2\text{Br}_2$, containing Jahn-Teller ion Cu^{2+} , which was considered earlier as a rare example of the Jahn-Teller system with localized electrons and e_g degeneracy with locally compressed ligand octahedra, must in fact have elongated octahedra with the long axes alternating in the basal plane. Thus, yet one more Jahn-Teller material turns out to be not an exception, but rather follows the general rule that the octahedra around such ions are elongated. This form of the Jahn-Teller distortions and orbital ordering should lead to strong ferromagnetic exchange in ab -plane, the interlayer exchange being very weak. The predicted crystal and magnetic structure should be observable by the de-

tailed structural and magnetic studies.

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